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SYNTHESIS OF USEFUL ELECTRONIC STRUCTURES USING
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DEPT OF ELECTRICAL ENGINEERING R M WALSER ET AL.
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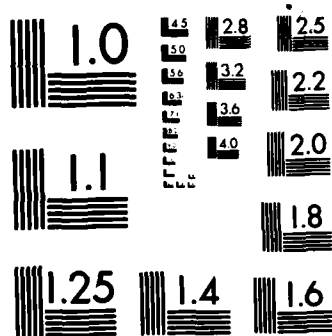
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FINAL REPORT: ONR CONTRACT N00014-75-C-0916

TITLE: Synthesis of Useful Electronic Structures Using Solid-Solid Phase Reactions Near Surfaces

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This final report is meant to be used in conjunction with all of the other technical articles and progress reports submitted over the duration of the contract. We are thus just summarizing the state of progress and disposition of several parts of this work as they existed at the end of this contract.

Work on first silicide formation has been done on various systems including Pd-Si, Pt-Si, Ni-Si, Co-Si, V-Si, Cr-Si, Ti-Si and Fe-Si.

In the Co-Si system, in addition to the work on first nucleation TED studies and the metal-insulator transition preceeding first nucleation (reprint of paper included), we have made ($\frac{1}{f}$) noise of thin films in the pre-nucleation regime. This work was started in an attempt to develop a technique for more accurate monitoring of structural changes in the non crystalline regime of prenucleation. It is felt that the fluctuation spectra will be a good monitor of such structural changes. The initial $\frac{1}{f}$ noise measurements on Co-Si thin films showed anomalous amplitude and current variation in the films which were in the prenucleation regime and at present this method appears very promising.

The work on the Fe-Si system was of a preliminary nature - in effect to monitor the limits of the prenucleation regime in terms of substrate doping and annealing temperature. Originally, this system was selected as the opti-

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mum system for magnetic measurements in an effort aimed at correlating the spin pairing-depairing transition with the prenucleation regime structural parameters. In the prenucleation study we found that several stages of prenucleation were observed via TED prior to FeSi nucleation, including an unidentified non crystalline phase with significant short range order. Also the FeSi nucleation temperature was reduced from the 450°C observed on weakly doped Si to room temperature or less on heavily As-doped substrates. This effect should probably be followed up on in more detail for other doped substrates. In addition, the magnetic studies still appear feasible and promising.

Significant measurements have been made on the Cr-Si and Ti-Si systems though the work here is also of a preliminary nature. The Cr-Si system is interesting because the first nucleated phase CrSi_2 is a semiconductor and the correlation of first nucleation with a metal-semiconductor transition of the prenucleation film would contribute significantly to the information about the generality of the results seen in the Co-Si case (and apparently in the Fe-Si case). The Ti-Si system is important because recent work has indicated (via X-ray diffraction) nucleation of a TiSi phase prior to what has been previously reported to be the first phase nucleated TiSi_2 . Our initial work has indicated the formation of a non equilibrium interstitial type phase prior to nucleation of TiSi_2 , but the TED results are not consistent with TiSi nucleation. This system is important as an interconnect system in emerging VLSI technology so that how it works is important.

Preliminary excess " $\frac{1}{f}$ " noise measurements on Co-Si thin film in the prenucleation to transition regime indicate anomalous behavior in both the magnitude of the noise and its variation with current in the low frequency regime. These initial results indicate that it would be fruitful to study

noise and perhaps dielectric response as an indication of structural evolution prior to 1st nucleation.

We have critically surveyed thin film nucleation studies done on metal-metal reaction couples. A comparison of the metal-metal systems with metal-semiconductor systems has indicated the first nucleation path in the all metal systems is also kinetically selected, but generally without the complication of "phase skipping" observed in the metal-semiconductor systems in concentration regions of easy glass formation.

We have also studied the role of interface disorder and oxygen on compound nucleation in the V/Si system. We specifically examined their role in the planar nucleation of V_3Si and VSi_2 formed by annealing (at 600-1000°C) thin sputter-deposited V films on crystalline Si. In summary, the results of our experiment indicate that VSi_2 nucleation cannot be suppressed unless both oxygen is present and the surface is disordered. In addition, bistable V_3Si and V_5Si nucleation is observed unless the disordered Si is less than some undetermined, but small, thickness. The results indicate that the role of oxygen is to retard Si recrystallization and bypass nucleation of the congruently melting compound VSi_3 .

PUBLICATIONS: (10/1/80 - 9/30/81)

1. R.W. Bené, R.M. Walser, G.S. Lee and K.C. Chen, "Is First Compound Nucleation at Metal-Semiconductor Interfaces an Electronically Induced Instability?", J. Va. Sci. Technol. 17 (5), 911 (1980).
2. R.W. Bené, "First Phase Nucleation in Metal-Metal Systems: A Comparison With Metal-Semiconductor Systems," (Submitted to J. Appl. Phys.).
3. L. Lancaster, R.M. Walser and R.W. Bené, "Study of Compound Formation by Annealing Sputter Deposited Thin Vanadium Films on Single-Crystal Substrates," (to be submitted to J. Appl. Phys.).

Is first compound nucleation at metal—semiconductor interfaces an electronically induced instability?

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We present transmission electron microscopy (TED) and transport measurements on thin films of cobalt on (100) and (111) silicon substrates which show that first phase nucleation proceeds upon deposition past a critical thickness and is preceded by a semiconductor/metallic transition in the glassy, as-deposited phase. We have also performed electron diffraction measurements on thin cobalt films deposited on highly doped Si substrates. It is found that compound nucleation begins upon metal deposition for any thickness down to practical minimum depositions for our sputtering system on the order of 10 Å. We interpret these results to indicate that in these systems thin film nucleation is driven by an electronic two-dimensional instability of the interphase region.

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I. INTRODUCTION

Thin films of transition metals react with single crystals of silicon to form silicides at temperatures roughly one-half the lowest eutectic temperature in the binary equilibrium phase diagram.¹ Most transition metals only form a single silicide phase (out of the many available on the phase diagrams) at these low temperatures, but several of the more noble transition elements (Pt, Ni, Co) form more than one such phase. Very little has been done of a modelling nature concerning second (or third) phase formation but we have introduced a rule for first phase nucleation² and have subsequently discussed³⁻⁵ a possible physical interpretation for the occurrence of this rule in Tm-Si and Tm-Ge systems. Basically, a glassy interphase region is thought to form prior to the first compound phase nucleation and this region acts as a membrane in controlling subsequent first phase nucleation. In an effort to learn more about the structures and events prior to first nucleation when a metal is deposited onto a single crystal substrate, we are studying the structure and transport properties of ultrathin films of transition metals on Si substrates. Our depositions are done in "technical" vacuums of the 10^{-7} Torr (1.33×10^{-12} Pa) range on substrates with different cleaning procedures, and thus our work should complement other work done at UHV. An important point to make, however, is that for many of the transition metals, the first compound nucleated is relatively independent of the cleanliness of the substrate. The large majority of the experiments have been on Si with relatively thick metal layers, but several studies of Si with ultrathin films have been carried out in several laboratories with the result that the first phase nucleated is the same in both situations. This is particularly true for the near noble transition metals where impurities such as oxygen may slow down the kinetics or change the grain structure, raise the reaction temperature, etc., but the first phase nucleated is usually the same. This is true to a much lesser extent in the more refractory metals where, for example, a significant amount of oxygen may severely limit the nu-

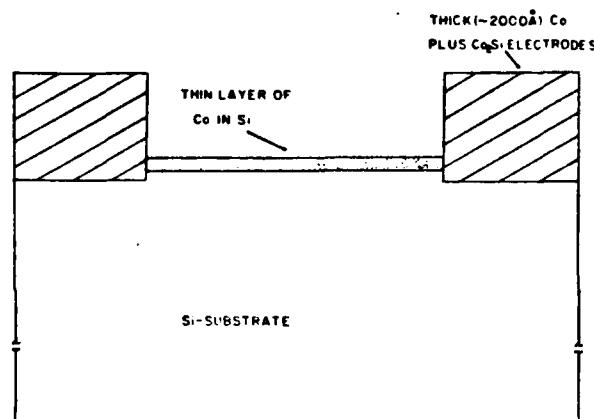


FIG. 1. Experimental structure for resistance measurement.

cleation rate of the favored silicide to such an extent that another more metal-rich phase is formed.^{6,7} Also it should be stressed here that these statements pertain to reactions between two thin films where selection of intermixing concentrations is part of the nucleation kinetics. If bulk glasses are prepared by splat/cooling for example, we may well have different compound nucleation depending on the concentrations of elements in the glass. For example, Pd_3Si has been reported to be formed upon heating of $\text{Pd}_{81}\text{Si}_{19}$ glass,⁸ and Fe_3Si_3 , FeSi , or FeSi_2 are formed upon heating of Fe_xSi_y glass in different composition ranges.⁹

In terms of our glassy interphase model, an invariance of first nucleation means that the addition of impurities at the interface may alter the concentration, extend the thickness, and change the reaction temperature of the glass to compound phase transition, but the basic reaction path is not changed.

In a previous study¹⁰ we have reported structure studies using transmission electron diffraction (TED) of thin films of Ni deposited on Si and SiO_2 substrates. In this work we saw

an amorphous phase at room temperature for Ni thicknesses below a critical value which depended upon substrate preparation (oxygen content, backsputtering, etc.). For Ni thicknesses greater than the critical value, Ni_2Si nucleation was observed upon deposition. In order to generalize our observations, we have made measurements on the Co-Si system; and also to determine more about the properties of the amorphous layer prior to first phase nucleation, we have monitored the surface resistance of the thin film. A preliminary version of some of these results has been previously reported.¹¹ Here we give a more detailed account of these experiments and report others which have subsequently been completed. In Sec. II, we discuss our experimental procedure, summarize the experimental results on Co deposited on 4-10 $\Omega\text{-cm}$ Si, and discuss the results in terms of the hypothesis¹¹ that first nucleation is an electronically driven instability in the glassy layer. We next test this assertion by considering experimental results of thin films of Co deposited on heavily doped Si substrates. We then discuss our conclusions concerning Co on Si and other systems in Sec. IV.

II. COBALT ON 4-10 $\Omega\text{ cm}$ SILICON

The Si substrates used are phosphorous-doped Si single crystal wafers with a resistivity of 4 to 10 $\Omega\text{ cm}$ and surfaces of either (100) or (111) orientation. The cleaning process for the polished wafers was accomplished by an ultrasonically agitating bath with organic solvents, followed by cleaning in a 10% HF solution and rinsing in high purity deionized water prior to loading into the sputtering apparatus. The vacuum system used is a conventional oil-diffusion pump with a LN cold baffle. After pumping the vacuum system to 10^{-7} Torr (10^{-12} Pa) ultrathin cobalt films are sputter deposited by sputtering the 3N cobalt target at 2 KV rf potential in 20 μ , 5N argon flow discharge. We made several different ultrathin cobalt films in sputtering times from 5 to 120 s, which correspond very approximately to thicknesses of 7-140 \AA . The deposition rate under this sputtering condition was obtained from interferometric measurements of the thickness of the deposited Co film with 30 min sputter deposition time. Of course, the deposition rate calibrated by this method will not be accurate for short time deposition (ultrathin film) because the sputtering conditions such as target temperature and substrate temperature will not reach their equilibrium, hence the thickness value of ultrathin film mentioned above is just for comparative reference.

For Transmission Electron Microscopy studies, the Co-Si substrates are ultrasonically cut into 3 mm-diam. specimens and thinned to a thickness less than 200 \AA from their backsides by a jet thinning machine. The etching solution for jet thinning is a mixture of 70% HNO_3 and 30% HF.

The sample structure for surface resistance measurements is shown schematically in Fig. 1. We use a mask to cover the center part of a rectangular Si substrate. The electrodes are sputter deposited onto the substrate first, then the mask is removed, and afterward ultrathin cobalt film is r.f. sputtered onto the Si surface. With this sample structure, two Schottky barrier contact electrodes leak insignificant current through Si substrates at low temperatures (below 100 K) compared to the $\approx 10^4 \Omega$ resistance at the metal-semiconductor transition



(a)



(b)

FIG. 2. TED diffused amorphous structure of (a) 20 s cobalt sputter deposition on 4-10 $\Omega\text{-cm}$ Si(100), (b) 60 s cobalt sputter deposition on 4-10 $\Omega\text{-cm}$ Si(111)

(operationally defined as $dR_s/dT = 0$). Thus, we can assume that the resistance we measure in the temperature ranges considered is the characteristic resistance of ultrathin film regions if they are near the phase transition (within about two to three orders of magnitude). In this case the four-point probe

measurement does not offer significant improvement in resolution of the resistance of the thin film since the Si substrate (via the Schottky barrier) will dominate these measurements until the transition. The resistance measurements in the range of $\approx 10^6 \Omega$ or above are not used for our present purposes due to the possible complicating effects of the large area Schottky barrier prior to very observable effects of substrate shunting near $10^8 \Omega$.

TED pictures of samples with sputter deposition times less than 60 s as seen in Fig. 2 show diffuse patterns on the silicon background which indicate amorphous structures of these ultrathin Co-Si films. Sheet resistance data of the same samples as seen in Fig. 3 show negative temperature coefficient of resistance (TCR) behavior, which indicates that these ultrathin films behave electrically like a semiconducting glass. As thicker films are deposited (sputtering times longer than 60 s) the TED pictures as seen in Fig. 4 show sharp polycrystalline ring patterns indicating Co_2Si nucleation. The corresponding sheet resistance data as seen in Fig. 3 shows zero to positive TCR which indicates metallic behavior. Thus, we conclude that the amorphous to crystallization transition is correlated with the semiconductor to metal transition in the Co-Si ultrathin film. The critical thickness where the films achieve metallicity and Co_2Si nucleation commences is dependent on substrate preparation and sputtering parameters and can generally be reduced to a smaller thickness if we backsputter the substrates before deposition. This seems reasonable as we may expect a surface region containing oxygen to be less metallic and a more stable glass. In addition, since the electronic transition appears gradually, and we have observed in our diffraction studies that the crystalline regions do not cover the entire surface, we hypothesize that nucleation is triggered by a local-delocal electronic phase transition in the glass phase. Also, the magnitude of the surface resistance at this transition ($\approx 10^4 \Omega/\square$) indicates we have achieved a two-dimensional (or less) metallic structure. This interpretation is based upon measurements of many types of films by us and also in the extensive literature on metal-semiconductor

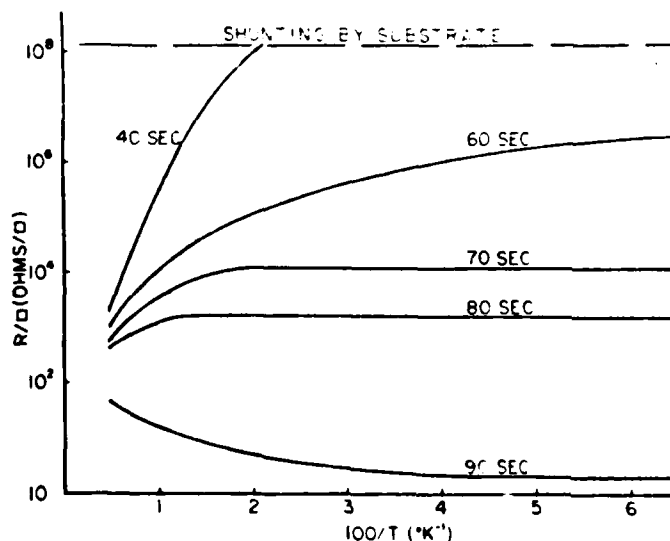


FIG. 3. Log of surface resistance vs $100/T$.



(a)



(b)

FIG. 4(a) TED Co_2Si polycrystalline structure of (a) 70 s cobalt sputter deposition on 4-10 Ω cm Si(111), 4(b) 90 s cobalt sputter deposition on 4-10 Ω cm Si(111).

transition, which show transitions in thin films and MOS inversion layers which depend on surface resistance rather than resistivity and which occur near $10^4 \Omega/\square$.

III. COBALT ON HEAVILY DOPED SILICON

In order to test the preceding hypothesis, we have made measurements on ultrathin films deposited on degenerately doped silicon substrates. The heavily doped silicon substrates used are Si(111) with phosphorous doped to resistivity

.001-.005 Ω -cm, Si(111) with arsenic doped to resistivity .0009-.015 Ω -cm, Si(111) and (100) with antimony doped to resistivity .005-.010 Ω -cm, and Si(111) with boron doped to resistivity .005-.016 Ω -cm. These silicon substrates are sputter deposited in the same way as the preceding (4-10 Ω -cm) silicon substrates.

We analyze these ultrathin cobalt films on heavily doped silicon substrates with the same methods as the 4-10 Ω -cm samples, with the exception of the resistance measurements. (The sample preparation procedures were identical. We just didn't make the extra structures for measuring the resistance.) Since these substrates are metallic in the temperature range 10-300 K, we cannot make Schottky barrier contact electrodes as we do in 4-10 Ω -cm substrates. We find from TED measurements that Co_2Si is nucleated on all heavily doped substrates we have used, and for all depositions down to the thinnest one (sputter deposition time 5 s) we can make. The result for a typical 20 s sputtering time sample is shown in Fig. 5. This TED pattern is further evidence that the first phase nucleation is induced by interfacial metallicity in the Tm-Si thin film system.

IV. SUMMARY OF RESULTS AND CONCLUSIONS

We have seen that ultrathin films of Co deposited on various Si substrates produce an amorphous layer until the films become metallic (defined by $dR_s/dT > 0$), whereupon Co_2Si is nucleated. In addition, Co films deposited upon heavily doped (highly conducting) Si substrates (four different dopants—both *p* and *n*-type) nucleate Co_2Si for all depositions down to the thinnest one we produced. These results strongly

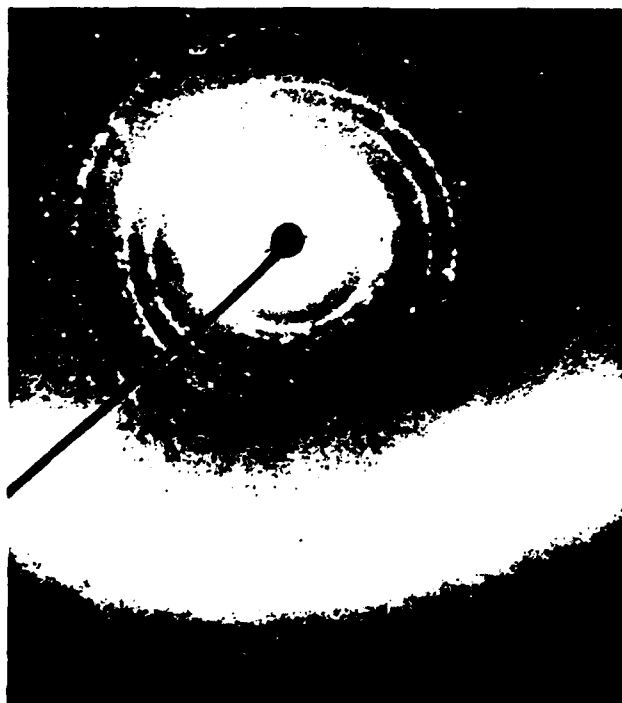


FIG. 5. TED Co_2Si polycrystalline structure of 20 s cobalt sputter deposition on arsenic heavily doped Si(111).

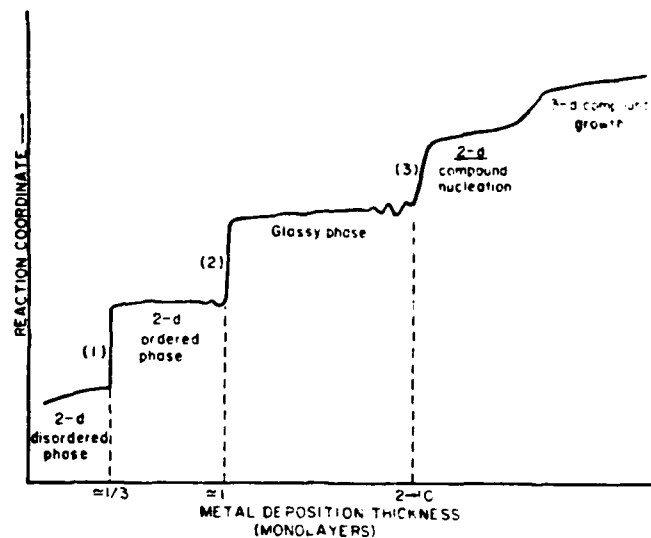


FIG. 6. Generalized possible reaction path sequence leading to first nucleation at subeutectic temperature.

indicate that Co_2Si nucleation at low temperatures is an electronically stimulated transition. (Note that we inferred this from our results on lightly doped Si, and this inference is strengthened by our measurements on heavily doped Si.) In addition, the value of the surface resistance where metallicity is achieved indicates that this required metallicity is two-dimensional in nature. Evidently island formation of the metal on Si was not a problem because we didn't see Co_2Si nucleation in any region until the whole surface structure achieved metallicity. An amorphous layer was not seen on the heavily doped substrates which, of course, does not mean that the system doesn't go through such a phase prior to first nucleation. The glassy region could well have a much lower reaction temperature and thickness. The only evidence we have is that the end product (i.e. the first phase nucleated) is the same in either case, and since apparently first nucleation in the silicides is reaction path determined (phase is not selected according to highest heat of formation), the reaction path is basically the same in either case. This is our second use of this "Basic Assumption" that the reaction path is importantly invariant if the phase selected for nucleation remains the same. To discuss what we mean by this we consider that there may be several "events" along the reaction path at fixed *T* and *P*, prior to first nucleation, schematically indicated in Fig. 6.

The plateaus are an indication that there may be many metastable structures prior to first nucleation. The vertical lines indicate the transitions between these structures. Of course, there may be many other possible reaction paths leading to other possible first phase nucleation; what we picture is the winning one—i.e., the fastest path. Now, in terms of this picture, the "Basic Assumption" is that any of the transitions may be absent (and thus the metastable state on either side) due to different substrate preparation, etc. except transition labelled 3. The position of this transition in terms of metal thickness, transition temperature, etc. may change without affecting first nucleation phase as long as it is not

perturbed to such an extent that some other reaction path becomes faster. Thus, in our terminology the basic reaction path is determined by the existence of transition 3 in the fastest reaction path. For the near noble metals on Si substrates at low temperatures, quite often (considering the large majority of the experimental data) this path is the fastest with or without substrate doping and whether we are at UHV or a good technical vacuum. Within our model the main effect of impurities is to change the (meta) stability of the surface glass. Our experiments reported here give evidence that transition 3 may be electronically driven over a surface which is less than three-dimensional. As a specific example we have indicated two-dimensional nucleation in Fig. 6. We also stress that phases such as the two-dimensional ordered phase prior to transition two may or may not exist for specific systems.

ACKNOWLEDGMENT

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the Air Force Office of Scientific Research (AFFC Contract F49620-77-C-0101).

¹The experimental work on compound formation in metal semiconductor systems is too voluminous to cite but typical examples are J. A. Borders and S. I. Picraux, *Proc. IEEE* **62**, 1224 (1974); H. Kräutle, M.-A. Nicolet, and J. W. Mayer, *J. Appl. Phys.* **45**, 3304 (1974).

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